#### **General Report:**

# Lewis & Clark Fund Grant and Early Career Collaboration Award

to

Dr. Roy Price, currently at SUNY Stony Brook, SoMAS, New York; formerly at University of Southern California, Los Angeles, California (at time of L&C grant only).

[This report is a summary of activity relating to the Lewis and Clark Fund Grant, and subsequently the Early Career Collaboration Award, received by Dr. Roy Price in order to investigate alkaline *shallow-sea* hydrothermal vents as analogs to early Earth environments important for origin of life.]

## **Background and Objectives**

On June 4<sup>th</sup>, 2012, Price received grant approval for his proposal "Expanding" frontiers for origin of life research: Serpentinite-hosted shallow-sea hydrothermal vents". The goal of this research was to travel to New Caledonia (South Pacific) to collect samples from the Prony Hydrothermal Field (PHF), a shallow-sea vent site with a 38 m carbonate hydrothermal edifice and active alkaline venting, similar to the Lost City Hydrothermal Field (LCHF), off-axis mid-ocean ridge. As pointed out in the proposal, the PHF and LCHF may be analogous to early-Earth serpentinizing environments where abiogenesis – the long ago switch from abiotic to biotic processes – may have occurred. Research of submarine, alkaline, serpentinizing hydrothermal systems has thus far been limited to the Lost City, and thus there is a fundamental lack of information for these important environments. Unfortunately, after receiving the funds, Price had difficulties in obtaining a sampling permit for collecting samples from the New Caledonia site. Unknown to him, a group of French scientists had started similar work to what was proposed. Due to overlap with thier research objectives, the permit was denied, and Price began negotiations with them to collaborate on another NASA-funded New Caledonia project focusing on aspects not being considered. At this point Price asked permission to switch the L&C funding to another, similar and perhaps more important, field site – the Strytan Hydrothermal Field (SHF), located in Eyjafjord, northern Iceland. Due to similarities between the two shallow-sea vent sites, we anticipated no significant changes in our sampling/analysis objectives, only a change in the location of the field site. For example, both sites exhibit very similar geochemical characteristics when compared to the Lost City, such as the discharge of a reduced, alkaline (pH ~10-11), warm (30-75 °C) hydrothermal fluid, which mixes with surrounding seawater to precipitate 35-55 m high porous mineral towers. Permission was granted, and the funds from the Lewis and Clark research grant were combined with funds already received from the National Science Foundation (CDEBI), and an expedition took place in July 2013.

Subsequently, progress was made with the French research team (called "HydroProny"), and Price submitted an Early Career Collaboration award proposal, which would allow him to travel to New Caledonia and begin the collaborative efforts with the HydroProny group. That proposal was granted, and an expedition took place in April/May 2014.

The objectives for each of these expeditions were to collect and analyze hydrothermal fluids and precipitates for geochemical characteristics in the context of the NASA Astrobiology roadmap, particularly the first three major Science Goals: (1)

understanding the nature and distribution of habitable environments in the universe, (2) exploring for habitable environments and life in our own Solar System, (3) understanding the emergence of life.

### Progress update for the Lewis and Clark Award

[The following text is from a manuscript in prep. All methods, tables, figures and most interpretations have been left out of this summary report. It is anticipated that the manuscript, currently entitled, "Low temperature alteration of basalt and H<sub>2</sub> / CH<sub>4</sub> production in a ridge-flank hydrothermal system: the shallow-sea, alkaline, Strytan Hydrothermal Field (SHF), Eyjafjördur, Iceland" will be submitted by the end of 2014.]

#### **Sampling**

An expedition to the Strytan Hydrothermal Field took place July 2013. The primary purpose of this study was to evaluate the geochemical signatures at the site that may result from low temperature 'serpentinization' of basalts, particularly  $H_2$  and  $CH_4$  concentrations and an evaluation of  $\delta^{13}C$  of the  $CH_4$  to evaluate biogenic vs. abiogenic production of  $CH_4$ . Preliminary samples for microbiology were also taken. Funding from the L&C were used entirely for supporting the SCUBA diving operations through the Strytan Diving Center. Additional logistical and scientific funds were obtained from the NSF Center for Deep Biosphere Interactions (CDEBI).

There are two main areas where cones and hydrothermal venting are present in Eyjafjord, and are referred to as "Arnarnesstrytan" and "Big Strytan" (Figure 1). Big Strytan was the first to be discovered, and is so called because of the presence of a very large cone, reaching up to 55 m height from the seafloor. There are series of other cones in the area of the Big Strytan, but our sampling only took place on the largest cone. Arnarnesstrytan is located north of Arnarnes, a small spit on the west side of the fjord. The system is comprised of several hydrothermal chimneys or clay-stacks forming a 500 m long line trending approximately north-south. Many individual and overlapping chimneys rise up to 10 m above the seafloor (Gautason et al., 2005). Another site, off of the island of Hrisey, which consists of hydrothermal fluid venting through horizontal cracks in basalt rocks with no cone development, was also sampled (Figure 2A). Abundant microbial mats were present where the hydrothermal fluids came into contact with overlying rocks.

During the second dive on July 9th at Arnarnesstrytan, Scuba divers noticed that, for unknown reasons, a small (~70 x 30 cm) cone was broken off, at approximately 20m water depth. Two days before, the cone was intact (Erlendur Bogason, pers. comm). We collected the cone for both microbiological and geochemical analyses, and this site was designated "A1". Subsequently, fluids were collected from the broken off area where the cone once existed. Site A2 was on a near-by large cone with significant fluid venting, and at a shallower depth (~12 m). Sites S1 and S2 were located on the biggest cone at Big Strytan (Figure 3B). S1 was located at ~24 m depth, on the rope side of the cone, to right of a blue rope used as a guide, and was a "big" vent, which has a focused vent opening of ~2" diameter. S2 was located above S1, at ~19 m depth. A single dive took place off the northeast point of the island Hrisey, and samples were taken for geochemistry using

syringes. Seawater was sampled for background geochemistry directly out from the Strytan Dive Center.

#### **Results**

#### Geochemistry

In total 5 sites were sampled for hydrothermal fluids during the expedition. Two from the Big Strytan area (S1 and S2), two from the Arnarnesstrytan area (A1 and A2), and one from Hrisey Island (H1). Temperatures ranged from 66.6 to 78.1°C, with the highest temperature measured at the A2 site. Hrisey temperatures measured 67.4°C, while the A1 and A2 sites were 66.6 and 78.1 °C, and the S1 and S2 sites were 72.1 and 73.4 °C, respectively. Various other temperature measurements where fluid samples were not taken fall within this range. The pH of the fluids at Hrisey ranged from 9.16 to 9.37, while the range for A1 (9.6 to 9.86), A2 (9.83 to 10.08), S1 (10.14 to 9.79), and S2 (9.91 to 10.22), all fall within a narrow range of values. The ambient seawater temperature was approximately 7 °C, and the pH was 8.12, and variability in both temperature and pH should be affected by seawater entrainment during sampling (i.e., a decrease in temperature and increase in pH should accompany seawater mixing). Thus, these values should be taken as minimum, relative to the deeper hydrothermal reservoir fluids.

Oxidation-reduction potential (ORP), which is the activity of all oxidizers and reducers in the solution relative to a platinum electrode (Myron-L meter), were always negative for samples from Arnarnesstrytan and Big Strytan (-76 (A2) to -160 (S1)), and positive for Hrisey (+103 to +156). A negative ORP indicates the ability to donate electrons; the higher the negative charge, the greater the ability to provide electrons and the more reducing the fluids. Thus, hydrothermal fluids from the SHS in general are highly reducing. Seawater ORP measured +217, and thus it is possible that the Hrisey site has mixed with oxidized seawater, either during or prior to sampling, or that the shallow-circulating source fluids are more oxygen-rich compared to the cone systems. Hrisey Island is very small, and it is thus likely that the fluids circulating through the system have not had adequate time to become reducing, and are still oxygen-rich.

Using TDS as an estimate of salinity, it is clear that the hydrothermal fluids from all sites, including the Hrisey site, were very dilute compared to seawater. For example, seawater TDS was 36450 ppm, while the range for the hydrothermal fluids were as follows, also in ppm: A1 (527 to 5758), A2 (305 to 3367), S1 (464 to 3781), S2 (300 to 2430), and Hrisey (1990 to 5106). Previously, Marteinsson et al. (2001) indicated that the Big Strytan fluids were primarily derived from meteoric water with low concentrations of major seawater salts and  $\delta^{18}$ O and  $\delta^{2}$ H ratios nearly identical to local precipitation. Our data agree with this evaluation, and it is likely that not only the Big Strytan site, but also the Arnarnesstrytan and Hrisey sites are derived from local meteoric water which penetrates through the ground, is heated up, and discharges into the fjord.

Sulfide measurements indicate low but significant concentrations, which at pH 9-10 is probably in the form HS and/or the completely deprotonated form S<sup>2</sup>. Hrisey concentrations were lowest, ranging from 0.1 to 0.5  $\mu$ M, while A1 and A2 (6.5 to 7.6 and 7.2 to 9.8  $\mu$ M, respectively) and S1 and S2 (11.9 to 12.5 and 11.9 to 12.4, respectively) were much higher. Note that concentrations at Arnarnesstrytan versus Big Strytan were consistently lower.